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Next 1 Page(s) In Document Denied

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"On the Action of Hexamethylcyclotrisilazane on Difunctional Phenols"

Plasticheskie Massy, (No. 4) 26 (1964)

In polymer literature (1) it is shown currently that the groups Si-N and Si-O-C normally interact in stoichiometric amounts as, for instance, polyalkylcyclosilazanes with difunctional alcohols such as ethylene glycol.

Earlier (2) a study was reported of the reaction of hexamethylcyclotetrasilazane with monofunctional phenols such as para, meta and orthocresols. (This) aroused interest in the (possible) reaction of hexamethylcyclotrisilazane with difunctional phenols.

Thus there has been carried out the interaction of hexamethylcyclotrisilazane and resorcinol, also hydroquinone, according to the equation:

$$n((CH_3)_2SiNH)_3 + 3n\ C_6H_4(OH)_2 \rightarrow$$

$$3\ H(-OC_6H_4OSi(CH_3)_2-)_nNH_2 + (3n-3)NH_3.$$

The reaction was accompanied by the evolution of ammonia and the formation of a dark colored glue-like polymer. The yields of polymer amounted to 61.4 and 65.1%. This small yield was accounted for by the sublimation of the difunctional phenols from the reaction mixture on heating.

The polymerization reaction (took place) in acetone solution, in benzene, toluene, chlorobenzene, cresols, but not in methanol (insoluble). As (shown in) figure 1 (there is) evidence of the relative change in viscosity as the polymerization process continues.

The work has also included studies on the properties of these polymers which responded to thermomechanical testing.

Thermomechanical property-relationships (studied by) V.A. Kargin, have definitely been calibrated to increase of temperature of 20° per minute, using samples of 50 g. and time of contact of the sample of 15 seconds. Thermomechanical studies showed that at the temperature range to -40° C. the polymers appeared to crystallize (brittle). The polymers from resorcinol shifted their brittle point to a highly plastic state at -35° to -30° and from this a region of the highly plastic state between -30° and -25°. For polymers from hydroquinone, this region covers the interval -40° to -35° C. and -35° to -20° C. (figure 2).

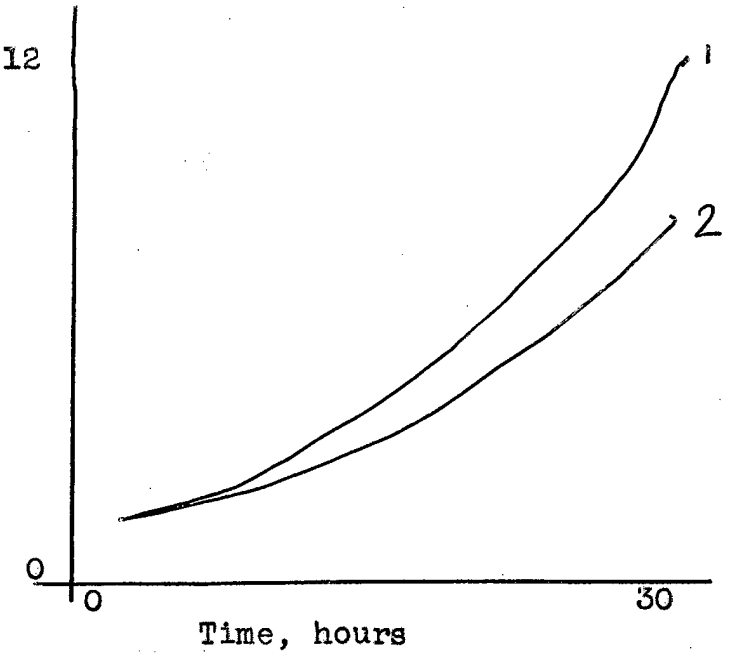


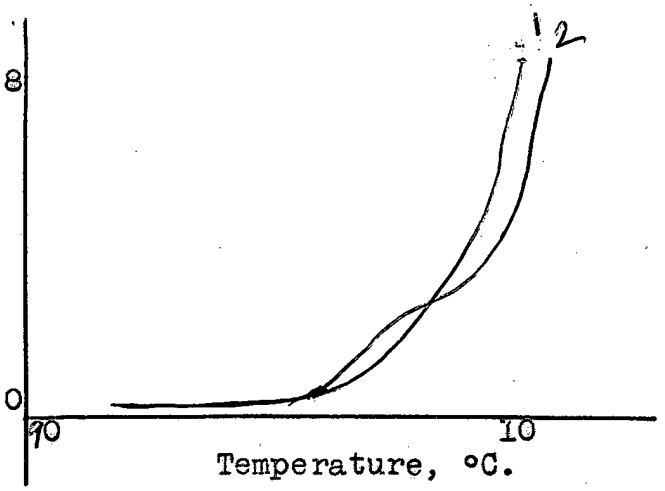
Figure 1

1. Change in relative viscosity during polymerization from the interaction of hexamethylcyclotrisilazane and resorcinol
2. Same for hydroquinone

The Interaction of Hexamethylcyclotrisilazane with Resorcinol

In a four necked flask, furnished with stirrer, trap, thermometer, capillary funnel and drainage tube, with a system for the absorption of ammonia, were placed 16.5 g. (0.15 mole) of resorcinol. There was added 10.9 g. (0.05 mole) of hexamethylcyclotrisilazane. The reaction was exothermic and proceeded with the production of ammonia.

This mixture was heated to 200° C. and the reaction continued at this temperature for 13 hours. The resorcinol sublimed. In the flask a rubber-like polymer remained. The yield was 15.3 g. (61.4%) of polymer. Found %: C 56.06; H 6.17; Si 17.36; N 0.52. Calculated for $H(OC_6H_4OSi(CH_3)_2)_nNH_2$, % C 57.83; H 6.11; Si 16.82; N 0.62. Molecular weight: found 2239.



Thermomechanical Behaviour of the Polymers from the Action of Hexamethylcyclotrisilazane and Resorcinol (1) and Hydroquinone (2)

The Interaction of Hexamethylcyclotrisilazane and Hydroquinone

(In air) in an analogous manner, 16.5 g. (0.15 mole) of hydroquinone was heated with 10.9 g. (0.05 mole) of hexamethylcyclotrisilazane for 15.5 hours at 220° C. then one hour at 250°C. giving 16.2 g. (65.1%) of polymer. Found, %: C 55; H 6.48; Si 18.16; N 0.55. Calculated for $H(OC_6H_4OSi(CH_3)_2)_nNH_2$, % C 57.83; H 6.11; Si 16.82; N 0.63. Molecular weight: found 2215.

Summary

The action of hexamethylcyclotrisilazane on resorcinol and hydroquinone occurs with rupture of the cyclic silazane, forming siloxyphenyl containing polymers and ammonia.

Bibliography

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2. K.A.Andrianov, M.V.Astanov and V.B.Losev, Izvestiya Akademii Nauk, SSSR, OKhN, 950 (1963)